The Nature of the *ortho* Effect. IV. Alkaline Hydrolysis of *ortho*-Substituted Benzoates

Marvin Charton

Contribution from the Department of Chemistry, Pratt Institute, Brooklyn, New York 11205. *Received June 13, 1968*

Abstract: The effect of *ortho* substituents upon the rates of alkaline hydrolysis of methyl and ethyl benzoates and upon the rates of methanolysis of 1-menthyl benzoates is purely electrical in nature; steric effects are not significant. The electrical effect is almost entirely a localized (field) effect. The results show that the assumptions underlying the definition of the Taft σ_o* constants are not warranted. The magnitude of the *ortho*-electrical effect is comparable to that of the *meta*- and *para*-electrical effects for these reactions.

In his definition of substitutent constants for *ortho* substituents, Taft[1] made use of the equations

$$\log (k_X/k_H)_A \equiv E^\circ_S \tag{1}$$

and

$$\log (k_X/k_H)_B \equiv E^\circ_S + 2.48\sigma_o^* \tag{2}$$

where the k's are rate constants for substituted and unsubstituted benzoate esters, respectively, A and B indicate acidic and basic ester hydrolysis, respectively, E°_S is a steric parameter characteristic of the *ortho* substituent, and σ_o* is a substituent constant characteristic of the electrical effect of the *ortho* substituent. We have previously shown[2,3] that the E°_S values are not a function of steric effects; in fact they are almost completely a measure of resonance effects, and may include a small localized (field and/or inductive) effect as well. In view of these results it seemed of interest to determine the nature of the *ortho*-substituent effect upon the basic hydrolysis of benzoate esters. To achieve this end we have correlated data taken from the literature with the equations

$$Q_X = \sigma_{I,X} + \sigma_{R,X} + r_{V,X} + h \tag{3}$$

$$Q_X = \sigma_{I,X} + \sigma_{R,X} + h \tag{4}$$

$$Q_X = \sigma_{I,X} + h \tag{5}$$

The substituent constants and van der Waals radii required for these correlations are taken from earlier papers in this series.[2,4] The sets studied are cited in Table I.[5] We have also examined rates of methanolysis of *ortho*-substituted 1-menthyl benzoates; for purposes of comparison, rate constants for the corresponding *meta*- and *para*-substituted benzoates were also studied. The correlations were carried out by means of multiple linear regression analysis. The value for X = H has been excluded from all the sets studied. We have shown elsewhere[6] that the unsubstituted compound cannot be considered a typical member of an *ortho*-substituted set.

Results

The results of the best correlations with eq 3 and 4 are presented in Table II; results of the correlations with eq 5 are set forth in Table III.

***ortho*-Substituted Sets.** Rates of alkaline hydrolysis of 2-substituted methyl benzoates at 35° and 45° gave poor and fair correlations, respectively, with eq 3 (sets O1 and O2). Correlations with eq 4 gave very good and excellent results, respectively (sets O1B, and O2B). Results of t tests show that α is the most significant regression coefficient. Correlation with eq 4 of the rates of alkaline hydrolysis of ethyl benzoates in acetone–water mixtures at 25 and 40° gave results which were not significant (sets O3B–O8B). The nonsignificance of these results is probably due to the fact that there are only four points in each of these sets. It is interesting to note that t tests again show α to be the most significant of the regression coefficients. Rates of alkaline hydrolysis of 2-substituted ethyl benzoates in 3% aqueous ethanol gave a poor but significant correlation (set O9) with eq 3. Excluding the value of X = NO_2 did not improve the results, probably because of the small size of the set (set O9A). Correlation with eq 4 gave results which were not significant (set O9B). Some improvement resulted from the exclusion of the value for X = NO_2 (set O9C). Correlation with eq 4 of the rates of alkaline hydrolysis of 2-substituted ethyl benzoates in 85% aqueous ethanol at 25, 35, and 50° (sets O10B–O12B) gave fair, poor, and poor results, respectively. Again, the results would probably have been better had the sets studied been larger. Rates of alkaline hydrolysis of 2-substituted ethyl benzoates in 65% and 85% aqueous dimethyl sulfoxide (sets O13B and O14B) when correlated with eq 4 gave poor but significant results. Once more, the small size of the set is the most likely cause of the poor results. We note that once again, for sets O10B–O14B, α is of far greater significance than is β. Correlation with eq 3 of the rates of methanolysis of 2-substituted 1-menthyl benzoates at 39.9 and 50° gave poor but significant results (sets O22 and O23). Correlation of these data with eq 4 gave very good results (sets O22B and O23B). Exclusion of the value for X =

(1) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley & Sons, Inc., New York, N. Y., 1956, p 565.
(2) M. Charton, *J. Am. Chem. Soc.*, **91**, 615 (1969).
(3) M. Charton, *ibid.*, **91**, 619 (1969).
(4) M. Charton, *J. Org. Chem.*, in press.
(5) Tables of the data used in the correlations and of the complete results of the correlations have been deposited as Document No. NAPS-00156 with the ASIS National Auxiliary Publication Service, % CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.
(6) M. Charton and B. I. Charton, *J. Org. Chem.*, **33**, 3872 (1968).

Table I. Sets Studied

Set	Reaction	Ref	Solvent	Temp, °C	n^{g}
1	$2XC_6H_4CO_2Me + OH^-$	*a*	80% v/v $MeOH-H_2O$	34.8–35	0
2		*a*		44.8–45	0
3	$2XC_6H_4CO_2Et + OH^-$	*b*	600 ml/l. of H_2O in MeAc	25	4
4		*b*		40	4
5		*b*	500 ml/l. of H_2O in MeAc	25	4
6		*b*		40	4
7		*b*	400 ml/l. of H_2O in MeAc	25	4
8		*b*		40	4
9		*c*	3% $EtOH-H_2O$	25	0
10		*d*	85% $EtOH-H_2O$	25	3
11		*d*		35	3
12		*d*		50	3
13		*e*	65% $DMSO-H_2O$	25	2
14		*e*	85%	25	2
15		*e*	95%	25	2
21	$2-(XC_6H_4CO_2)_2-1-C_{10}H_{20} + MeO^-$	*f*	MeOH	30	4
22		*f*		39.9	4
23		*f*		50	4

[a] N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1291 (1963). [b] E. Tommila, J. Paasivirta, and K. Setala, *Suomen Kemistilehti*, **B33**, 187 (1960). [c] M. Hojo, M. Utaka, and Z. Yoshida, *Kogyo Kagaku Zasshi*, **23**, 1034 (1965). [d] D. P. Evans, J. J. Gordon, and H. B. Watson, *J. Chem. Soc.*, 1430 (1937). [e] M. Hojo, M. Utaka, and Z. Yoshida, *Kogyo Kagaku Zasshi*, **23**, 1040 (1965). [f] R. W. Taft, Jr., M. S. Newman, and F. H. Verhoek, *J. Am. Chem. Soc.*, **72**, 4517 (1950). [g] In $10^n k_2$.

NO_2 gave poor results (sets O22C and O23C). Correlation of the data for this reaction at 30° with eq 4 gave results which were not significant (set O21B). Again, α seems to be more significant than β or ψ.

As in general the data seem to show a greater dependence on σ_I than on σ_R or r_V as shown by the t tests for the significance of α, β, and ψ, correlations were made with eq 3. Of the 18 sets of data studied, 7 gave very good, 7 gave fair, and 2 gave poor but significant correlations with eq 3 (see sets in Table III). Two sets (O4D and O15D) did not give significant correlations with eq 3. Exclusion of the value for X = NO_2 gave poorer results for set O9D (set O9E). Set O15D gave an excellent correlation with the σ_p constants with $\rho = 2.59 = \alpha = \beta$; $h = 1.99$; $r = 0.9999994$; $t = 950.3$; $s = 0.00101$; $s_\rho = 0.00272$; $n = 3$; $CL = 99.9$.

We conclude from these results that *in general the alkaline hydrolysis of ortho-substituted benzoate esters is subject only to electrical substituent effects and is independent of steric effects.* We further conclude that the electrical effect in general is largely if not entirely a localized effect.

meta-**Substituted Sets.** Rates of alkaline hydrolysis of 3-substituted ethyl benzoates in 85% aqueous ethanol at 25 and 35° gave poor but significant correlations with eq 4 (sets M10 and M11). Rates of methanolysis of 3-substituted 1-methyl benzoates at 30, 39.9, and 50° gave excellent, poor, and excellent correlation, respectively, with eq 4 (sets M21, M22, and M23).

para-**Substituted Sets.** Correlation with eq 4 of rate constants for alkaline hydrolysis of 4-substituted ethyl benzoates in aqueous acetone gave excellent results (sets P3, P4, and P7) as did rate constants in 3% aqueous ethanol (set P9) and in 65 and 83% aqueous dimethyl sulfoxide (sets P13 and P14). Rate constants for the methanolysis of 4-substituted 1-menthyl benzoates at various temperatures all gave excellent correlations with eq 4.

Discussion

Nature of the *ortho*-Substituent Effect. Our results, in particular, the correlation with eq 5, show that eq 2 is not obeyed. Rates of alkaline hydrolysis and of methanolysis of 2-substituted benzoates are independent of steric effects. They are largely or entirely a function of σ_I. We may rationalize the nature of the substituent effect upon basic ester hydrolysis in the following manner. It has been shown that proton transfers such as the ionization of 2-substituted pyridinium ions[7] and the rates of H–D exchange of 2-substituted benzenes in liquid ammonia[8] are largely or entirely a function of the localized effect. In terms of the parameter, ϵ, defined as

$$\epsilon \equiv \beta/\alpha \tag{6}$$

which serves as a measure of the composition of substituent effects, the above reactions show a value of ϵ = 0–0.3. Most of the sets studied in this paper show values of ϵ in this range. The attack of a hydroxide ion on the carbonyl carbon of the ester is formally analogous to the attack of some base on the proton transferred in the ionization of a pyridinium ion, or in H–D exchange.

The lack of a significant dependence on σ_R observed for most of the sets studied may also be indicative of the location of the transition state on the reaction coordinate. If the transition state is located such that the bond between the hydroxide (or methoxide) ion and the carbonyl group is largely formed, no significant delocalization is possible between the ring and the reaction site. This may account at least in part for the small contribution of σ_R in the over-all substitutent effect.

Magnitude of the Substituent Effect. The average value of α for alkaline hydrolysis obtained from those 2-substituted sets which gave significant correlations with eq 5 is 2.50. This is comparable to the average values of α of 2.38 and 2.28 obtained for alkaline hydrolysis from the 3- and 4-substituted sets. The average value of α for the methanolysis obtained from the 2-substituted sets is 2.06, comparable to the average values of 2.52 and 2.58 obtained from the 3- and 4-sub-

(7) M. Charton, *J. Am. Chem. Soc.*, **86**, 2033 (1964).
(8) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 156 (1963).

Table II. Results of Correlations with Eq 3 and 4

Set	α	β	ψ	h	R	F	r_{12}	r_{13}	r_{23}
O1	2.15	−0.373	−0.579	−0.852	0.999	113.8	0.612	0.0946	0.834
O1B	1.83	−1.35		−1.98	0.998	252.7	0.612		
O2	1.59	−2.54	0.668	−2.98	0.989	30.92	0.687	0.0224	0.730
O2B	1.97	−1.41		−1.69	0.989	66.75	0.687		
O3B	2.71	0.432		0.790	0.966	7.012	0.048		
O4B	1.83	1.04		1.85	0.903	2.196	0.048		
O5B	2.74	0.451		0.663	0.966	7.048	0.048		
O6B	2.57	0.385		1.16	0.962	6.243	0.048		
O7B	2.81	0.523		0.605	0.967	7.203	0.048		
O8B	2.64	0.465		1.12	0.966	7.061	0.048		
O9	2.41	1.89	−1.61	0.819	0.979	15.63	0.524	0.735	0.791
O9C	2.00	1.21		−2.06	0.925	5.964	0.178		
O10C	2.53	−0.0403		−0.998	0.999	212.7	0.061		
O11B	2.46	−0.0650		−0.580	0.998	159.7	0.061		
O12B	2.33	−0.153		−0.00801	0.997	80.94	0.061		
O13B	2.13	0.838		−0.0329	0.998	162.8	0.390		
O14B	2.24	1.55		0.754	0.996	61.63	0.390		
O21B	1.90	0.887		−1.22	0.990	24.16	0.333		
O22	1.79	0.274	0.201	−1.23	0.997	58.23	0.374	0.697	0.871
O22B	1.92	0.537		−0.842	0.996	135.9	0.374		
O23	1.76	0.256	0.200	−0.834	0.997	62.21	0.374	0.697	0.871
O23B	1.89	0.517		−0.451	0.996	142.0	0.374		
O23C	1.79	0.348		−0.477	0.996	58.22	0.224		
M10	2.42	1.20		−0.154	0.999	192.7	0.207		
M11	2.34	1.18		0.277	0.999	191.1	0.207		
M21	2.59	1.04		−0.223	0.998	355.4	0.104		
M22	1.73	1.83		0.714	0.929	9.490	0.104		
M23	2.45	0.992		0.558	0.998	348.1	0.104		
P3	2.23	2.30		1.66	0.999995	53,763.0	0.207		
P4	2.15	2.22		2.13	0.999999	312,500.0	0.207		
P7	2.47	2.34		1.46	0.9999	7,812.0	0.303		
P9	1.52	1.46		−1.51	0.992	87.26	0.104		
P13	2.40	2.32		0.587	0.999	392.6	0.140		
P14	2.77	2.86		1.24	0.9998	2,544.0	0.140		
P21	2.65	2.55		−0.253	0.9992	1,299.0	0.247		
P22	2.58	2.47		0.144	0.9992	1,260.0	0.247		
P23	2.51	2.39		0.528	0.9992	1,213.0	0.247		

Set	s_{est}	s_α	s_β	s_ψ	s_h	n	CL
O1	0.0606	0.534	1.67	0.977	1.91	5	90.0
O1B	0.0498	0.136	0.226		0.0448	5	99.0
O2	0.155	1.39	3.97	2.31	4.48	6	95.0
O2B	0.129	0.300	0.588		0.104	6	99.5
O3B	0.352	0.729	0.723		0.379	4	<90.0
O4B	0.475	0.983	0.976		0.511	4	<90.0
O5B	0.355	0.735	0.729		0.382	4	<90.0
O6B	0.353	0.731	0.725		0.379	4	<90.0
O7B	0.360	0.746	0.741		0.388	4	<90.0
O8B	0.342	0.710	0.704		0.369	4	<90.0
O9	0.197	0.489	0.478	0.468	0.887	6	90.0
O9C	0.344	0.781	0.566		0.372	5	<90.0
O10B	0.0671	0.123	0.166		0.0683	4	95.0
O11B	0.0753	0.138	0.186		0.0767	4	90.0
O12B	0.100	0.184	0.248		0.102	4	90.0
O13B	0.0744	0.149	0.181		0.0810	4	90.0
O14B	0.146	0.292	0.353		0.158	4	90.0
O21B	0.161	0.319	0.634		0.184	4	<90.0
O22	0.0886	0.299	0.537	0.378	0.730	5	90.0
O22B	0.0710	0.139	0.171		0.0772	5	99.0
O23	0.0839	0.284	0.509	0.358	0.692	5	90.0
O23B	0.0680	0.133	0.164		0.0739	5	99.0
O23C	0.0677	0.166	0.234		0.0781	4	90.0
M10	0.0811	0.134	0.325		0.0614	4	90.0
M11	0.0786	0.130	0.315		0.0595	4	90.0
M21	0.0669	0.105	0.139		0.0493	6	99.9
M22	0.3421	0.536	0.710		0.252	6	90.0
M23	0.0640	0.100	0.133		0.0471	6	99.9
P3	0.00490	0.00808	0.0196		0.00371	4	99.5
P4	0.00196	0.00324	0.00786		0.00149	4	99.5
P7	0.0204	0.0335	0.0318		0.0149	5	99.9
P9	0.0955	0.150	0.199		0.0703	6	99.5
P13	0.0707	0.115	0.149		0.0520	5	99.5
P14	0.0329	0.0536	0.0692		0.0242	5	99.9
P21	0.0499	0.0745	0.0962		0.0363	7	99.9
P22	0.0492	0.0735	0.0949		0.0358	7	99.9
P23	0.0487	0.0727	0.0939		0.0354	7	99.9

Table II (*Continued*)

Set	t_α	CL	t_β	CL	t_ψ	CL	t_h	CL
O1	3.881	80.0	0.223	<20.0	0.593	20.0	0.446	20.0
O1B	13.46	99.0	5.973	95.0			39.76	99.9
O2	1.144	50.0	0.640	20.0	0.289	20.0	0.665	20.0
O2B	6.567	99.0	2.398	90.0			16.25	99.9
O3B	3.717	80.0	0.598	20.0			2.084	50.0
O4B	1.862	50.0	1.066	50.0			3.620	80.0
O5B	3.728	80.0	0.619	20.0			1.736	50.0
O6B	3.516	80.0	0.631	20.0			3.061	50.0
O7B	3.767	80.0	0.706	20.0			1.559	50.0
O8B	3.718	80.0	0.661	20.0			3.035	50.0
O9	4.928	95.0	3.954	90.0	3.440	90.0	0.923	50.0
O9C	2.561	80.0	1.817	50.0			5.538	95.0
O10B	20.57	95.0	0.024	<20.0			14.61	95.0
O11B	17.83	95.0	0.035	<20.0			7.562	90.0
O12B	12.66	90.0	0.717	20.0			0.079	<20.0
O13B	14.30	95.0	4.630	80.0			0.406	20.0
O14B	7.671	90.0	4.391	80.0			4.772	80.0
O21B	5.956	80.0	1.399	50.0			6.630	90.0
O22	5.987	80.0	0.510	20.0	0.532	20.0	1.685	50.0
O22B	13.81	99.0	3.140	90.0			10.91	99.0
O23	6.197	80.0	0.503	20.0	0.559	20.0	1.305	50.0
O23B	14.21	99.0	3.152	90.0			6.103	95.0
O23C	10.78	90.0	1.487	50.0			6.108	80.0
M10	18.06	95.0	3.692	80.0			2.508	50.0
M11	18.00	95.0	3.746	80.0			4.655	80.0
M21	24.67	95.0	7.482	90.0			4.523	80.0
M22	3.228	95.0	2.577	90.0			2.833	90.0
M23	24.50	99.9	7.459	99.0			11.85	99.0
P3	276.0	99.0	117.3	99.0			447.4	99.0
P4	663.6	99.9	282.4	99.0			1430.0	99.9
P7	73.73	99.9	73.58	99.9			97.98	99.9
P9	10.13	99.0	7.337	99.0			21.48	99.9
P13	20.87	99.9	15.57	99.9			11.29	99.0
P14	51.68	99.9	41.33	99.0			51.24	99.9
P21	35.57	99.9	26.51	99.9			6.970	99.0
P22	35.10	99.9	16.03	99.9			4.022	98.0
P23	34.53	99.9	25.45	99.9			14.92	99.9

Table III. Results of Correlation with Eq 5

Set	α	h	r	t	s_{est}	s_α	n	CL
O1D	2.33	−1.85	0.962	6.135	0.176	0.379	5	99.0
O2D	2.47	−1.53	0.967	7.641	0.192	0.323	6	99.0
O3D	2.69	0.625	0.954	4.490	0.290	0.600	4	95.0
O4D	1.78	1.46	0.778	1.753	0.489	1.01	4	70.0
O5D	2.72	0.490	0.953	4.453	0.295	0.610	4	95.0
O6D	2.55	1.01	0.951	4.363	0.282	0.584	4	95.0
O7D	2.78	0.405	0.950	4.307	0.312	0.646	4	95.0
O8D	−2.62	0.940	0.951	4.365	0.290	0.600	4	95.0
O9D	1.81	−2.50	0.788	2.560	0.424	0.708	6	90.0
O9E	2.26	−2.57	0.787	2.207	0.458	1.02	5	80.0
O10D	1.53	−0.990	0.999	28.34	0.0488	0.0891	4	99.0
O11D	2.46	−0.567	0.998	23.86	0.0564	0.103	4	99.0
O12D	2.33	−0.0224	0.996	15.30	0.0834	0.152	4	99.0
O13D	2.40	−0.288	0.965	5.192	0.250	0.462	4	95.0
O14D	2.74	0.283	0.915	3.209	0.463	0.855	4	90.0
O15D	1.81	1.41	0.696	0.969	0.689	0.187	3	20.0
O21D	2.05	−1.39	0.970	5.598	0.196	0.366	4	95.0
O22D	2.09	−1.01	0.978	8.134	0.141	0.257	5	99.0
O23D	2.04	−0.611	0.979	8.276	0.136	0.247	5	99.0

stituted sets. Thus the magnitude of the substituent effect is approximately the same for *ortho*, *meta*, and *para* substitution. This is in sharp contrast to the *ortho* effect upon the ionization of benzoic acids in water, where α for the 2-substituted acids is more than twice α for the 3- and 4-substituted acids.

The Taft σ_o^* Constants. The Taft σ_o^* constants are defined by the equation[1]

$$\frac{1}{2.48}\left[\log\left(\frac{k_X}{k_H}\right)_B - \log\left(\frac{k_X}{k_H}\right)_A\right] \equiv \sigma_o^* \qquad (7)$$

The argument for eq 7 rests on the assumptions implicit in eq 1 and 2, that is, as follows. (1) The acidic hydrolysis of 2-substituted benzoates is a function largely or entirely of steric effects. (2) The basic hydrolysis of 2-substituted benzoates is a function of the *ortho*-electrical effect and a steric effect. (3) The steric effect is at least approximately the same in the acidic and basic hydrolyses; therefore in eq 7 the steric effect cancels out leaving the *ortho*-electrical effect.

In the previous paper of this series[3] we have disproven assumption 1 and therefore assumption 3 as well. In this paper we have disproven assumption 2. *Thus the Taft σ_o* constants do not represent an intrinsic general ortho-electrical effect.* They are a combination of the electrical effect in acidic hydrolysis, largely resonance in character, and the electrical effect in basic hydrolysis, largely localized in character. That their composition (as measured by ϵ) is the same as that of the σ_p constants is purely fortuitous. Their success in correlating many sets of *ortho*-substituted data is due to the variability of the *ortho*-electrical effect which ranges from $\epsilon = 0$ to $\epsilon = 2$. We will expand on this point in another paper.

Solvent Effects on the Composition of the *ortho*-Electrical Effect. We have shown elsewhere that when the pK_a values of 2-substituted benzoic acids in various solvents are correlated with eq 4, α is constant whereas β is a function of solvent.[5] The results obtained in aqueous acetone at 25° suggest the possibility of a solvent dependence of β for the correlations obtained with the rates of alkaline hydrolysis of 2-substituted ethyl benzoates. More telling evidence on this point is obtained from a consideration of the β values obtained for 65, 85, and 95% aqueous dimethyl sulfoxide. The β values are 0.838, 1.55, and 2,59, respectively. While the results are certainly not conclusive, they do indicate the strong possibility that β is a function of solvent for the alkaline hydrolysis of benzoate esters.

As was the case for the benzoic acid ionization, α seems to be largely or entirely free of solvent dependence.

Infrared Intensities as a Quantitative Measure of Intramolecular Interactions. V.[1] *ortho*- and *meta*-Disubstituted Benzenes. The ν_{16} Band near 1600 cm^{-1}

A. R. Katritzky,[2] M. V. Sinnott,[2] T. T. Tidwell,[2,3] and R. D. Topsom[4]

Contribution from the School of Chemical Sciences, University of East Anglia, Norwich, England, and the School of Physical Sciences, La Trobe University, Melbourne, Australia. *Received June 26, 1968*

Abstract: The integrated intensity is reported for the 1600-cm^{-1} band for many *meta*- and *ortho*-disubstituted benzenes. Equations relating the expected intensities with $\sigma_R{}^\circ$ parameters for the substituents are deduced and shown to hold. Conformational isomerism for *meta*-substituted benzaldehydes and other compounds with asymmetrical substituents is discussed and tentative values for the corresponding equilibrium constants are calculated. Steric and mesomeric interactions in *ortho*-disubstituted compounds are discussed.

Previous papers in this series have shown that the total integrated area of the bands near 1600 and 1580 cm^{-1} for mono-[5] and *para*-disubstituted benzenes[1] and for monosubstituted durenes[5] are related by eq 1, 2, and 3 to the $\sigma_R{}^\circ$ value(s) of the substituent(s); in eq 2 the algebraic signs of the $\sigma_R{}^\circ$ values result in over-all addition for "unlike" substituents and over-all subtraction for "like" substituents. The different values of the coefficients in eq 1, 2, and 3 (also 11; see later) are believed to arise from variations in the precise form of the normal mode as between various substitution types of benzenes. Equation 2 applies to *para*-disubstituted

$$A_{\text{mono}} = 17{,}600(\sigma_R{}^\circ)^2 + 100 \quad (1)$$

$$A_{para} = 11{,}800(\sigma_R{}^\circ 1 - \sigma_R{}^\circ 2)^2 + 170 \quad (2)$$

$$A_{\text{durene}} = 11{,}300(\sigma_R{}^\circ)^2 - 30 \quad (3)$$

compounds in which direct resonance interaction between the two substituents does not occur; discrepancies from eq 2 are useful for the investigation of substituent interactions.[1] Equation 3 applies in the absence of steric effects.

The extension of such infrared intensity measurements to other polysubstituted systems was expected to be a useful means for the examination of the combined effects of resonance and steric interaction. For example, *meta* substituents should be incapable of direct interaction either sterically or by ordinary conjugation, whereas *ortho* substituents can interact by both such means. Earlier semiquantitative work by one of us[6] had indicated that whereas the intensity of the *para*-disubstituted derivatives varied as the algebraic difference between the electronic effects of the substituents[7] the intensity of the *meta*-disubstituted compounds varied as approximately their sum,[8] and the *ortho*-disubstituted derivatives showed intermediate behavior.[9] Little other work has appeared on the

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(2) School of Chemical Sciences, University of East Anglia, Norwich, England.
(3) Department of Chemistry, University of South Carolina, Columbia, S. C.
(4) School of Physical Sciences, La Trobe University, Melbourne, Australia.
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